

Improved Performance and Safety of Lithium Ion Cells with the Use of Fluorinated Carbonate-Based Electrolytes

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ABSTRACT

There has been increasing interest in developing lithium-ion electrolytes that possess enhanced safety characteristics, while still able to provide the desired stability and performance. Toward this end, our efforts have been focused on the development of lithium-ion electrolytes which contain partially and fully fluorinated carbonate solvents. The advantage of using such solvents is that they possess the requisite stability demonstrated by the hydrocarbon-based carbonates, while also possessing more desirable physical properties imparted by the presence of the fluorine substituents, such as lower melting points, increased stability toward oxidation, and favorable SEI film forming characteristics on carbon. Specifically, we have demonstrated the beneficial effect of electrolytes which contain the following fluorinated carbonate-based solvents: methyl 2,2,2-trifluoroethyl carbonate (MTFEC), ethyl-2,2,2-trifluoroethyl carbonate (ETFEC), propyl 2,2,2-trifluoroethyl carbonate (PTFEC), methyl-2,2,2',2',2'-hexafluoro-*i*-propyl carbonate (MHFPC), ethyl-2,2,2',2',2'-hexafluoro-*i*-propyl carbonate (EHFPC), and *di*-2,2,2-trifluoroethyl carbonate (DTFEC). These solvents have been incorporated into multi-component ternary and quaternary carbonate-based electrolytes and evaluated in lithium-carbon and carbon-LiNi_{0.8}Co_{0.2}O₂ cells (equipped with lithium reference electrodes). In addition to determining the charge/discharge behavior of these cells, a number of electrochemical techniques were employed (i.e., Tafel polarization measurements, linear polarization measurements, and electrochemical impedance spectroscopy (EIS)) to further characterize the performance of these electrolytes, including the SEI formation characteristics and lithium intercalation/de-intercalation kinetics. In addition to their evaluation in experimental cells, cyclic voltammetry (CV) and conductivity measurements were performed on select electrolyte formulations to further our understanding of the trends in stability and ionic mobility imparted by different alkyl substituents in linear carbonates.

INTRODUCTION

There has been increasing interest in developing lithium-ion battery electrolytes that possess enhanced safety characteristics, while still being able to provide the desired stability and performance. Halogenated solvents have received some attention with the expectation that they will result in the desired improvements. In support of the concept of utilizing halogenated carbonated derivatives for lithium-ion batteries applications, Shu and coworkers¹ have reported using chloroethylene carbonate as an electrolyte solvent for lithium-ion batteries.^{2,3} The use of chloroethylene carbonate enabled the use of PC as a co-solvent for applications with highly graphitic electrodes without high rates of electrolyte decomposition. The film formed from the decomposition of chloroethylene carbonate was observed to be sufficiently stable that exfoliation of graphite was not observed in the presence of PC. The same group also investigated fluoroethylene carbonate electrolytes in the context of lithium ion batteries with graphite anodes.⁴

Recently, it has been demonstrated that lithium can be intercalated within graphite in trifluoropropylene carbonate (3-trifluoromethyl-2,5-dioxo-cyclopentan-1-one).^{5,6} Lithium intercalation within graphite has also been studied in an electrolyte solution consisting of 1.0 M LiClO₄ in trifluoropropylene carbonate (TFPC).⁷ The electrochemical behavior of graphite electrodes has also been studied in electrolytes consisting of 1.0 M LiClO₄ with EC+DEC and fluoroester-mixed EC+DEC solutions at low temperature to evaluate the effect of addition of fluoroesters on the electrochemical characteristics.⁸ Fluoroesters have also been studied by Shu *et al.* with the intent of improving the low temperature characteristics and suppress the dendrite formation on lithium anodes.⁹ The group studied a number of electrolyte formulations which were prepared using 25 mL of a fluoroester with 50 mL of a 1.0 M LiClO₄ EC+DEC (1:1) electrolyte. Conductivity and cyclic voltammetric measurements have also been performed on electrolyte formulations containing fluoro-carbonate solvents for Li-ion cells, however, no cell data was presented.¹⁰

In addition to the reports of using halogenated carbonates and esters, Besenhard and coworkers have been issued a patent¹¹ relating to the use of partially fluorinated ethers in lithium ion battery applications. The fluorinated ethers reported in the patent include compounds of the formulae $\text{RO}(\text{CH}_2)_m\text{O}_n\text{CF}_2\text{CFHX}$ (I) and/or $\text{XCFHCF}_2\text{O}(\text{CH}_2)_m\text{O}_n\text{CF}_2\text{CFHX}$ (II). It was recognized that these compounds impart greater safety aspects to lithium ion systems, as well as, resulting in batteries with improved low temperature performance.

In this paper we would like to describe our recent results relating to the development of lithium-ion electrolytes which contain partially fluorinated carbonate solvents. Specifically, we have demonstrated the beneficial effect of electrolytes which contain the following fluorinated carbonate-based solvents, illustrated in Fig. 1: methyl 2,2,2-trifluoroethyl carbonate (MTFEC), **1**, ethyl-2,2,2-trifluoroethyl carbonate (ETFEC), **2**, propyl 2,2,2-trifluoroethyl carbonate (PTFEC), **3**, methyl-2,2,2',2',2'-hexafluoro-*i*-propyl carbonate (MHFPC), **4**, ethyl-2,2,2',2',2'-hexafluoro-*i*-propyl carbonate (EHFPC), **5**, and *di*-2,2,2-trifluoroethyl carbonate (DTFEC), **6**.

In addition to investigating the use of partially and fully fluorinated carbonates, we have also investigated the use of partially fluorinated carbamates as lithium-ion battery electrolyte co-solvents. The compounds investigated include: 2,2,2-trifluoroethyl *N,N*-dimethyl carbamate (TFECm), **7**, and hexafluoro-*i*-propyl *N,N*-dimethyl carbamate (TFPCm), **8**. The chemical structures of these compounds are also shown below in Fig. 1

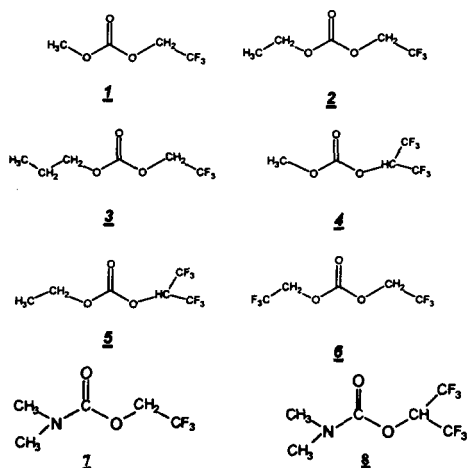


Fig. 1. Chemical structures of the partially fluorinated carbonate and carbamate solvents investigated.

One potential advantage of using partially fluorinated carbonate and carbamate solvents is that they possess the requisite stability demonstrated by the hydrocarbon-based carbonates, while also possessing more desirable physical properties imparted by the

presence of the fluorine substituents, such as lower melting points, increased stability toward oxidation, and favorable SEI film forming characteristics on carbon. In addition, these solvents can lead to the development of safer lithium ion batteries, due to their low flammability. In order to assess their viability, these co-solvents were blended (20-50 vol/%) in ternary and quaternary electrolyte formulations with the traditional cyclic and aliphatic carbonates.

EXPERIMENTAL

Ternary and quaternary electrolyte mixtures with ethylene carbonate (EC) as a base solvent were prepared with salt concentrations ranging from 0.50 M to 1.0 M. The carbonate-based solvents (EC, DMC, and DEC) were of battery-grade purity and were purchased with the desired concentrations of LiPF_6 salt from Mitsubishi Chemicals and were certified to contain < 50 ppm H_2O content. The partially fluorinated solvents described in the study were synthesized at the University of Southern California by known techniques.

Assessment of candidate electrolytes were evaluated in ~ 600 mAh experimental half-cells, consisting of O-ring-sealed, glass cells and contained jelly rolls of carbon electrodes as the cathode materials and lithium metal as the anode materials. In addition to half-cell studies, selected electrolytes were evaluated in experimental full-cells (350-450 mAh-size) consisting of MCMB carbon anode electrodes, $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode electrodes, and Li metal reference electrodes.

Electrochemical measurements were made using an EG&G Potentiostat/Galvanostat interfaced with an IBM PC, using Softcorr 352. A Solartron 1255 Frequency Response Analyzer was used with this potentiostat for impedance measurements, with M388 software. Charge-discharge measurements and cycling tests were performed with an Arbin battery cyclor.

RESULTS AND DISCUSSION

Charge/discharge characteristics

In order to effectively evaluate the potential of such solvents, electrolyte formulations were investigated in both Li-MCMB carbon and MCMB carbon- LiNiCoO_2 experimental cells. As shown in Fig. 2, excellent capacities were observed in Li-MCMB cells with a number of fluorinated carbonate-containing electrolyte formulations being comparable to non-halogenated solutions.

One aspect of studying the charge/discharge characteristics of the lithium metal-carbon half-cells included the determination of the irreversible and reversible capacities as a function of electrolyte type. When the first discharge of the lithium metal-carbon cells (or first lithium intercalation of carbon) were compared for the partially fluorinated carbonate-based electrolytes, they were all observed to behave in a

similar fashion adopting potentials indicative of lithium intercalation early in the cell discharge process, suggesting efficient SEI formation. When the initial potential decay profile is examined in more detail and compared with the baseline electrolyte, it was observed that the fluorinated solvent-containing electrolytes display nearly identical characteristics. This suggests that there is no compatibility problem associated with the incorporation of such solvents into electrolyte formulations, which is supported by the observed high coulombic efficiencies (89-92%) obtained during the first formation cycle of the electrolytes studied.

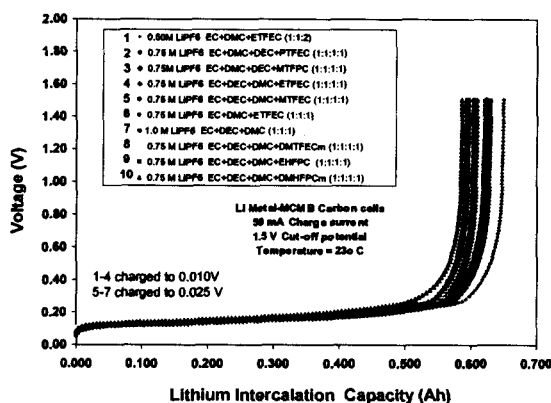


Fig. 2. Fifth lithium de-intercalation of lithium-MCMB cells with different carbonate-based electrolytes (25 mA to 1.5V).

When the cells containing the fluorinated co-solvent based electrolytes were compared in terms of the reversible capacity after five formation cycles, the following trend was observed in decreasing reversible capacity: 0.50 M LiPF₆ EC+DMC+ETFE (1:1:2) > 0.75M LiPF₆ EC+DEC+DMC+PTFEC (1:1:1:1) > 0.75M LiPF₆ EC+DEC+DMC+MTFPC (1:1:1:1) > 0.75M LiPF₆ EC+DEC+DMC+MTFEC (1:1:1:1) > 1.0M LiPF₆ EC+DEC+DMC (1:1:1) > 0.75M LiPF₆ EC+DEC+DMC+ETFE (1:1:1:1). The cells were initially subjected to five formation cycles at room temperature, which consisted of charging at 50 mA to a 1.5V cut-off and discharging at 50 mA (~C/12 rate) to 0.025 V (or 0.010 V, as indicated) followed by constant potential discharge for an additional 3-5 hours. The cells displayed stable capacity over the first five formation cycles, being comparable to the baseline carbonate solutions.

Charge/discharge Characteristics at Low Temperature

In addition to characterizing these cells in terms of the reversible capacity, the discharge/charge characteristics were evaluated as a function of temperature. When the MCMB electrodes were charged (intercalated) at room temperature and discharged at low temperature (-20°C) (de-intercalated) excellent capacity was observed in most cases ranging from 80% to 95% of the room temperature capacity, as shown in Fig. 3. It is evident that the electrolyte 0.75M LiPF₆

EC+DEC+DMC+ETFE delivered superior performance compared to the other formulations investigated including the baseline electrolyte (1.0M LiPF₆ EC+DEC+DMC (1:1:1)). In addition to displaying higher capacity, a significant decrease in the electrode polarization was also observed (> 200 mV decrease) with the ETFEC-based electrolyte containing cell. Comparable performance to the baseline electrolyte was displayed by the 0.75M LiPF₆ EC+DEC+DMC+PTFEC (1:1:1:1) formulation, which delivered almost equivalent capacity and had similar polarization effects. When the cell containing the 0.75M LiPF₆ EC+DEC+DMC+ETFE (1:1:1:1) electrolyte was charged at -20°C (carbon delithiated) 96.8 % of the room temperature capacity was delivered. The displayed trends suggest that the ethyl-2,2,2-trifluoroethyl carbonate containing electrolyte has higher conductivity at lower temperatures compared with the propyl 2,2,2-trifluoroethyl carbonate containing electrolyte due to the decreased viscosity effects. The fact that the ethyl-2,2,2-trifluoroethyl carbonate containing cell also displayed lower electrode polarization upon discharge suggests that the electrolyte has better filming properties on the MCMB electrodes.

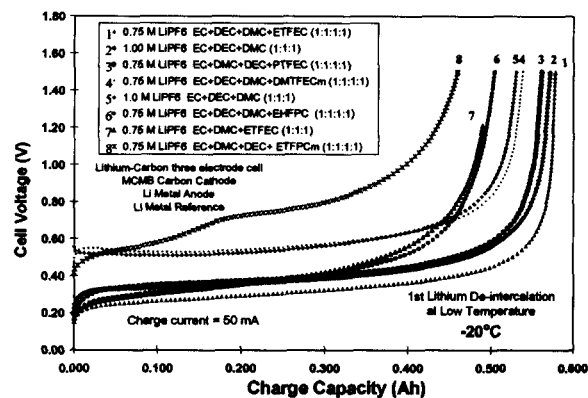


Fig. 3. Lithium de-intercalation of MCMB electrodes at low temperature (-20°C) in contact with various electrolytes. Cells were charged at 50 mA (~C/12) to a 1.5 V cut-off.

The capacities delivered at -20°C illustrated in Fig. 3 resulted from the room temperature charging (lithiation) of the carbon electrode prior to equilibrating the cell at low temperature. When the cells were allowed to cycle continuously at low temperature (-20°C), thus, the lithiation step occurring at low temperature, the discharge capacities observed were somewhat lower. This is illustrated in Fig. 4, in which the capacities of the cells were compared on the second cycle at -20°C, following a cell discharge at low temperature (carbon lithiation). As shown, the cell containing the 0.75M LiPF₆ EC+DEC+DMC+ETFE (1:1:1:1) electrolyte dramatically outperformed the other cells, displaying more than three times the capacity. These results suggest that in addition to possessing the desired physical properties (i.e., high conductivity and wide

liquid range) the ETFEC-containing electrolytes produce superior surface films on carbon allowing for rapid lithiation kinetics at low temperatures.

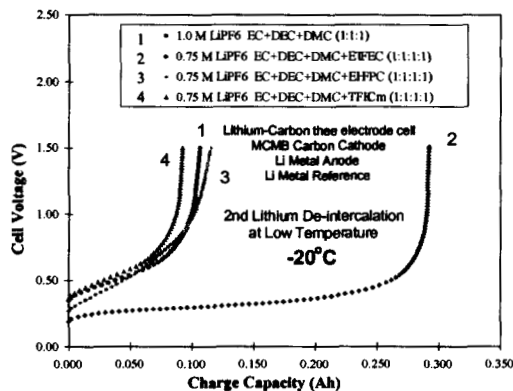


Fig. 4. Lithium de-intercalation of MCMB electrodes at low temperature (-20°C) in contact with different electrolytes following lithium intercalation at -20°C . Cells were charged at 50 mA ($\sim\text{C}/12$) to a 1.5 V cut-off.

In the course of the charge/discharge characterization, it was generally observed that the process of lithiation into carbon is less facile than the de-intercalation process (and is rate limiting), implying that the charge time and rate are crucial to obtain good performance at low temperature. The differences in the capacities of the different cells (where the carbon electrodes were charged at -20°C) can be understood by the relative charge acceptance at low temperature.

A.C. Impedance Results

In addition to studying the charge/discharge characteristics of these cells, a.c. impedance was used to probe the nature of the anode passivating film. Measurements were conducted for each cell after the formation process (5 cycles), as well as, after the cells had been subjected to cycling and characterized in terms of the self-discharge behavior. AC impedance measurements were also taken at a number of temperatures (25, 0, and -20°C) to determine the impact of temperature upon the film resistance of the samples. It was generally observed that the film resistance dramatically increased upon going to lower temperatures. These results suggest that the nature of the SEI layer on the carbon electrode plays a significant role in determining the low temperature discharge performance similar to the bulk resistivity of the electrolyte. When the impedance spectra of the cells containing the partially fluorinated carbonate-based electrolytes were compared to the baseline alkyl carbonate electrolytes at room temperature after the formation cycles, the electrodes in contact with the modified electrolytes generally displayed low film polarization characteristics as determined from the low R_{ct} values observed. Of the new electrolyte formulations investigated, the fluorinated carbonates

displayed superior characteristics to that of the carbonate-based solutions.

When impedance measurements were performed on the cells at low temperatures, dramatically lower film resistances were observed for the fluorinated carbonate-based electrolyte containing cells when compared with standard carbonate-based mixtures. When the cells were evaluated at 0°C , nearly a fourfold decrease in the film resistance was observed with some of the fluorinated carbonate-containing electrolytes compared to the baseline ternary solution. This can be mainly attributed to the desirable SEI film properties, which were produced in the formation cycles as a result of the reductive decomposition of the solvents and salts. The observed low film and charge transfer resistances of the fluorinated carbonate-containing cells at low temperature implies that more facile lithium kinetics occur. This trend is consistent with the charge/discharge performance at low temperature as described above. When the cells were evaluated for EIS response at -20°C , as shown in Fig. 5, the improvement over the baseline electrolyte was even more dramatic, with nearly an eightfold decrease in the film resistance values observed with the fluorinated carbonate-containing electrolytes.

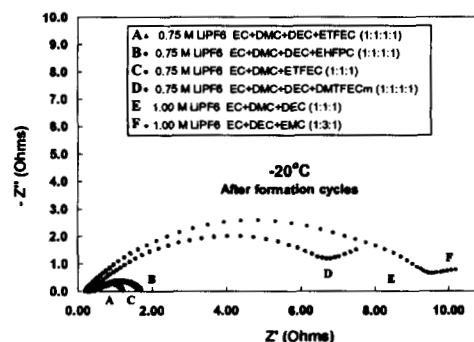


Fig. 5. AC impedance (Nyquist) plots of lithium-MCMB carbon cells possessing various electrolytes at -20°C after the formation cycles.

DC micropolarization results

DC micropolarization techniques were also employed to study the charge transfer behavior of the passivating films on the MCMB electrodes at various temperatures. The polarization resistance values of the electrodes were calculated from the slopes of the linear plots generated under potentiodynamic conditions at scan rates of 0.02 mV/s. The polarization resistance was consistently lower for the cells possessing fluorinated carbonate-containing electrolytes compared to the alkyl-carbonate-based systems, being especially dramatic at low temperatures, as shown in Fig. 6. Of the novel co-solvents studied, the ethyl 2,2,2-trifluoroethyl carbonate-based systems yielded the lowest polarization values, correlating well with the charge-discharge characteristics previously mentioned. As shown in Fig. 6, the cell containing 0.75M LiPF_6 EC+DEC+DMC+ETFE (1:1:1:1) resulted in a polarization resistance value

(1.531 kOhm) more than six times lower than that of the baseline electrolyte 1.00M LiPF₆ EC+DEC+DMC (1:1:1) (10.1 kOhm) at -20°C.

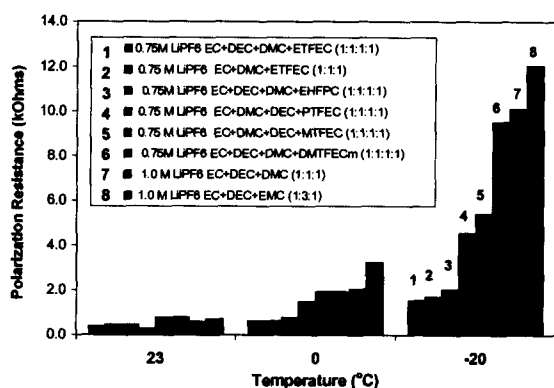


Fig. 6. Linear polarization resistance calculated from DC micropolarization plots of MCMB-carbon electrodes with different electrolytes at various temperatures.

Tafel micropolarization results

The lithiation/de-lithiation kinetics were also determined by conducting Tafel polarization measurements of the lithium de-intercalation process on the MCMB electrodes in contact with the various electrolytes. These measurements were conducted on the lithium-MCMB carbon cells at various temperatures (25, 0, and -20°C). When the cells were evaluated at -20°C, the electrolyte containing the partially fluorinated carbonate co-solvents resulted in the least amount of electrode polarization and the highest current densities implying facile lithium intercalation/de-intercalation kinetics. These results are consistent with the trends observed when the cells were evaluated using linear polarization techniques, as well as, the cell charge/discharge characteristics at low temperature.

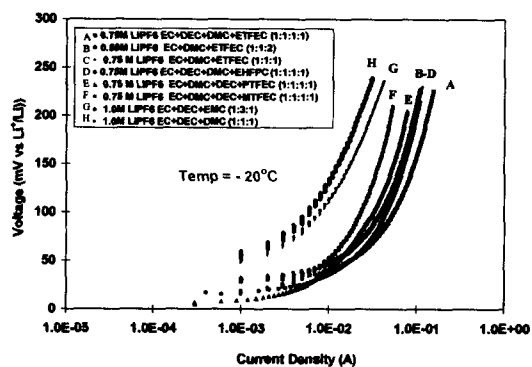


Fig. 7. Tafel polarization measurements performed on MCMB-carbon electrodes in contact with different electrolytes at -20°C.

Experimental Full-Cell (MCMB Carbon-LiNiCoO₂) Results

In addition to the above half-cell studies, selected electrolytes were evaluated in experimental full cells (MCMB Carbon-LiNiCoO₂) to fully assess the electrochemical compatibility with the desired high voltage couple. For example, a *di*-trifluoroethyl

carbonate-based electrolyte was incorporated into an experimental full cell (MCMB carbon-LiNiCoO₂) and good reversibility was observed, as shown in Fig. 8.

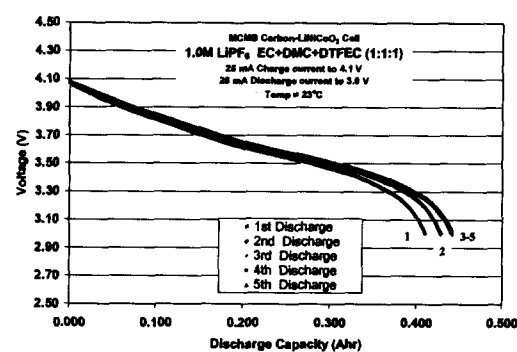


Fig. 8. First five discharge curves of a MCMB Carbon-LiNi_xCo_{1-x}O₂ cell at room temperature containing 1.0 M LiPF₆ EC+DMC+DTFEC (1:1:2).

Di-2,2,2'-2',2'-trifluoro ethyl carbonate (DTFEC) is an especially attractive co-solvent in that both alkyl substituents are partially fluorinated. This is conjectured to enhance the oxidative stability of the compound, as well as, decrease the flammable properties of the solvent resulting in inherently safer electrolytes (and thus safer lithium-ion batteries). When electrochemical characterization was performed on the cell containing 1.0 M LiPF₆ EC+DMC+DTFEC (1:1:1), excellent anode kinetics were observed (presumably due to favorable SEI layer formation) displaying higher limiting current densities at all temperatures investigated. A detailed description of the charge/discharge characteristics of full cells containing the fluorocarbonate-based electrolytes, and the corresponding electrochemical characterization, will be communicated in a future publication.

In order to fully investigate the viability of potential electrolyte formulations, tests have been performed in which the experimental test cells are subjected to high temperature exposure (60°C) for prolonged periods (10 days). Given that full electrochemical characterization of the cell was performed prior to the storage test, added insight can be gained in understanding the nature of irreversible capacity loss in lithium-ion cells when subjected to high temperature extremes or long storage periods (it is likely that the degradation modes are similar for both conditions). When the cell containing the fluorinated carbonated-based electrolyte was subjected to high temperature exposure good reversible capacity and a low self-discharge rate was observed, with ~ 84% of the initial capacity being utilizable after being stored at 60°C for 10 days in a full state of charge.

CONCLUSIONS

Partially fluorinated carbonate solvents have been incorporated into multi-component ternary and quaternary lithium battery electrolytes and their

beneficial performance demonstrated in experimental half- (Li metal-MCMB carbon) and full- (MCMB carbon-LiNiCoO₂) cells. A number of electrolyte formulations were prepared based upon the incorporation of a partially fluorinated aliphatic carbonate, including solutions containing (1) methyl 2,2,2-trifluoroethyl carbonate (MTFEC), (2) ethyl-2,2,2-trifluoroethyl carbonate (ETFEC), (3) propyl 2,2,2-trifluoroethyl carbonate (PTFEC), (4) methyl-2,2,2,2',2',2'-hexafluoro-*i*-propyl carbonate (MHFPC), (5) ethyl-2,2,2,2',2',2'-hexafluoro-*i*-propyl carbonate (EHFPC), and (6) *di*-2,2,2-trifluoroethyl carbonate (DTFEC). Excellent reversibility was generally observed, with most of the formulations resulting in higher reversible capacity after the formation cycles compared to the baseline electrolyte formulations in experimental half-cells. Good low temperature performance was also observed in many cases, with ETFEC- and PTFEC-containing cells performing the best. In addition to evaluating the cells in terms of their charge-discharge properties, a number of electrochemical techniques were used to determine the lithium intercalation/de-intercalation kinetics and the nature of the passivating films on the respective electrodes. When the impedance spectra (EIS) of the cells containing the partially fluorinated carbonate-based electrolytes were compared to the baseline alkyl carbonate electrolytes, the electrodes in contact with the novel electrolytes generally displayed low film polarization characteristics as determined from the low R_{ct} values observed, especially at low temperature. This suggests that candidate co-solvents investigated are not only compatible with the electrodes investigated, but are also involved in the fundamental film forming processes during initial activation and result in SEI layers with favorable characteristics (good lithium kinetics and a protective nature). The polarization resistance (calculated from linear polarization measurements) was consistently lower for the cells possessing fluorinated carbonate-containing electrolytes compared to the alkyl-carbonate-based systems, being especially dramatic at low temperatures. In addition, when Tafel polarization measurements were performed the electrolyte containing the partially fluorinated carbonate co-solvents resulted in the least amount of electrode polarization and the highest limiting current densities implying facile lithium intercalation/de-intercalation kinetics. These results are consistent with the trend observed when the cells were evaluated using linear polarization techniques, as well as, the cell charge/discharge characteristics at low temperature.

In addition to concept validation in experimental half cells, full cells were also fabricated containing electrolytes possessing the fluorinated carbonate solvents. Excellent reversibility was obtained the cells being comparable, if not exceeding, the reversible

capacity of the baseline formulation. While carrying out characterization tests, it was also observed that a cell with a fluorinated carbonate-containing electrolyte displayed good resilience to high temperature storage and minimal capacity loss. This is also encouraging, in that it suggests that these electrolyte formulations have good long term stability and will result in long-life lithium-ion cells. Further work is in progress to fully appreciate the promise of these advanced electrolyte formulations. Lastly it must be emphasized that these advanced electrolyte formulations will result in safer lithium batteries, due to the reduced flammability of a number of the electrolyte solutions reported herein.

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